Supporting Information for

A Catalytic Cycle for Oxidation of *tert*-Butyl Methyl Ether by a Double C–H Activation-Group Transfer Process

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Experimental Section

All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with Ar gas followed by passage through an activated alumina column.[1] Hexamethyldisiloxane and *tert*-butyl methyl ether were distilled from CaH_2 and degassed prior to use. (PNP)Ir=C(H)O^{t}Bu (**1**)[2] and 2,6-diisopropylphenylazide[3] were prepared according to literature procedures. Azidotrimethylsilane was purchased from Aldrich and degassed prior to use. Other reagents were purchased from commercial vendors and used without further purification.

Elemental analyses were carried out at Desert Analytics, Tucson, Arizona. NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent. ^{31}P NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4. Infrared spectra were recorded using a Perkin Elmer Spectrum BXII spectrometer. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker KAPPA APEX II diffractometer.

Photolysis reactions were performed in pyrex vessels with 450W medium-pressure mercury arc lamp (Ace Glass) or a 120V/23W halogen bulb, which produced essentially identical results.

X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Structures were determined using direct methods with standard Fourier

techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure.

(PNP)Ir–N_2 (3). A 50 mL pressure tube was charged with (PNP)Ir=C(H)O^{t}Bu (**1**) (42.0 mg, 0.0594 mmol) dissolved in toluene (15 mL). The solution was frozen and the headspace evacuated and backfilled with nitrous oxide (1 atm). Upon melting, the color of the solution changed from purple to orange over a period of 5 min. The solution was allowed to warm to ambient temperature, stirred for 15 min, and volatiles were removed in vacuo to afford an orange film. Lyophilization of the residues from benzene (5 mL) afforded **3** as a flocculent pale orange powder (37.9 mg, 98%). Orange crystals of **3** suitable for X-ray diffraction were obtained by slow evaporation of pentane from a concentrated solution. Due to its moderate light sensitivity, complex **3** was stored at –35 °C in the dark to prevent decomposition. ^{1}H NMR (C_6D_6): δ 7.69 (dt, J_1 = 8.7 Hz, J_2 = 2.1 Hz, 2H, Ar–*H*), 6.94 (m, 2H, Ar–*H*), 6.76 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 2H, Ar–*H*), 2.33 (m, 4H, –C*H*$(CH_3)_2$), 2.18 (s, 6H, Ar–C*H*$_3$), 1.32 (dvt, 12H, –CH(C*H*$_3)_2$), 1.12 (dvt, 12H, –CH(C*H*$_3)_2$. ^{13}C{^{1}H} NMR (C_6D_6): 164.1, 132.0, 131.6, 125.5, 121.7, 116.0, 26.4 (m), 20.3, 19.1, 18.4. ^{31}P{^{1}H} NMR (C_6D_6): δ 46.9 (s). IR (THF, KBr, cm^{-1}) υ(N_2): 2067. Anal. Calcd. for $C_{26}H_{40}IrN_3P_2$: C, 48.13; H, 6.21; N, 6.48. Found: C, 48.57; H, 5.69; N, 6.15.

Preparation of *tert*-butyl formate from complex (1). In a sealed NMR tube, a purple solution of **1** (ca. 15 mg) in C_6D_6 was frozen and the headspace evacuated and backfilled with nitrous oxide (1 atm). As the solution thawed, a gradual change in color from purple to pale yellow was observed. After 15 min, the disappearance of **1** was confirmed by NMR spectroscopy, and quantitative conversion to **3** and *tert*-butylformate was inferred as these were the only species

observed in the ^{1}H NMR spectrum (cf. Figures S1 and S2). ^{1}H NMR (*tert*-butyl formate, C_6D_6): δ 7.64 (s, 1H, –C(O)*H*), 1.24 (s, 9H, –C(C*H*$_3$)$_3$). The identity of the *tert*-butylformate organic product was confirmed by comparison to an authentic sample obtained from Aldrich.

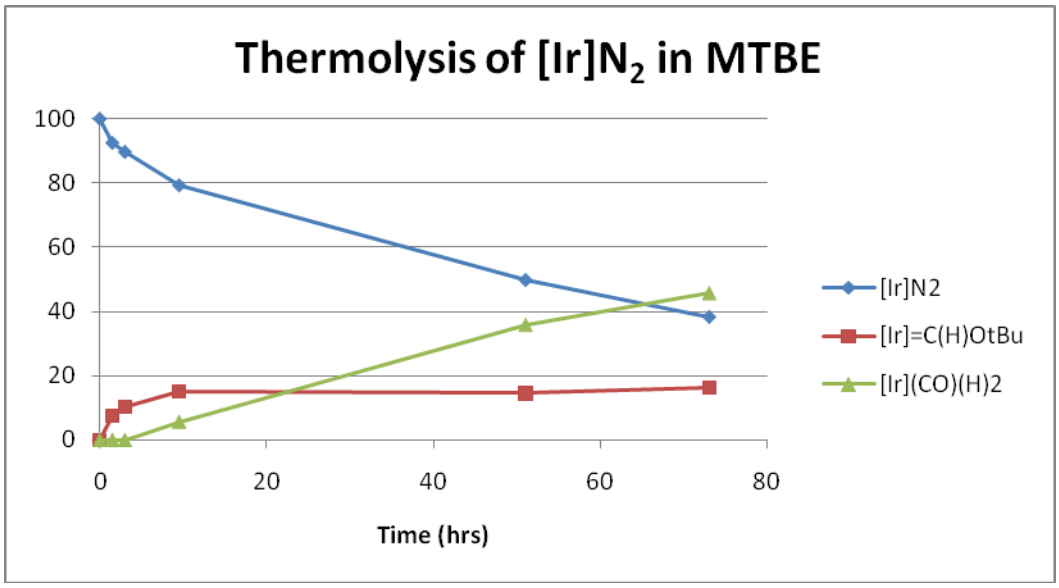
Preparation of *tert*-butyl *N*-(2,6-diisopropylphenyl)formimidate from complex (1). 2,6-diisopropylphenyl azide (6.1 mg, 0.030 mmol) was added in one portion to a solution of **1** (21.5 mg, 0.0304 mmol) in C_6D_6 (800 μL), causing an immediate change in color from purple to golden. After 15 min, the disappearance of **1** was confirmed by NMR spectroscopy, and quantitative conversion to **3** and *tert*-butyl *N*-(2,6-diisopropylphenyl)formimidate was inferred as these were the only species observed in the ^{1}H NMR spectrum. ^{1}H NMR (*tert*-butyl *N*-(2,6-diisopropylphenyl)formimidate, C_6D_6): δ 7.32 (s, 1H, –C(NDIPP)*H*), 7.25 – 7.10 (m, 3H, Ar–*H*), 3.26 (septet, $^3J_{HH}$ = 6.9 Hz, 2H, –C*H*(CH$_3$)$_2$), 1.45 (s, 9H, –C(C*H*$_3$)$_3$), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 12H, –CH(C*H*$_3$)$_2$). IR (C_6D_6, KBr, cm^{-1}) υ(C=N): 1669. The *tert*-butyl *N*-(2,6-diisopropylphenyl)formimidate organic product was identified by comparison of the distinctive spectral data, namely the ^{1}H chemical shift of the formimidate proton and the energy of the medium-intensity C=N infrared stretch, to those of analogous formimidate complexes.[2,4]

Preparation of *tert*-butyl *N*-adamantylformimidate from complex (1). 1-azidoadamantane (3.8 mg, 0.021 mmol) was added as a solid to a solution of **1** (13.1 mg, 0.0185 mmol) in C_6D_6 (800 μL). Over a period of 15 min, the solution gradually lightened from purple to brown. Conversion to **3** and *tert*-butyl *N*-adamantylformimidate was complete in 2 h, and the yield of formimidate was judged to be quantitative by ^{1}H NMR via integration versus an internal standard of hexamethyldisiloxane. ^{1}H NMR (*tert*-butyl *N*-adamantylformimidate, C_6D_6): δ 7.46 (s, 1H, –

C(NAd)*H*), 1.96 (m, 3H, –C*H* (Ad)), 1.67 (d, $^{3}J_{HH}$ = 2.7 Hz, –NC(CH_2)$_3$ (Ad)), 1.58 (m, 6H, –CH_2 (Ad)), 1.49 (s, 9H, –C(CH_3)$_3$).

Preparation of *tert*-butyl *N*-trimethylsilylformimidate from complex (1). Trimethylsilyl azide (2.5 μL, 0.019 mmol) was added in one portion to a solution of **1** (11.5 mg, 0.0163 mmol). No immediate color change was observed. After 10 h at ambient temperature, nitrene transfer to generate **3** and *tert*-butyl *N*-trimethylsilylformimidate was 25% complete, as judged by ^{1}H and ^{31}P NMR. Extended heating (8 h, 70 °C) brought about the complete consumption of **1**, though competitive degradation of **1** was noted at elevated temperatures (ca. 18% at 70 °C), as previously described.[5] Addition of large excesses (> 10 equiv) of trimethylsilyl azide to solutions of **1** followed by 12 h of reaction at ambient temperature and 4 h at 70 °C also facilitated the complete consumption of **1** and formation of **3** and *tert*-butyl *N*-trimethylsilylformimidate without decomposition. ^{1}H NMR (*tert*-butyl *N*-trimethylsilylformimidate, C_6D_6): δ 7.64 (s, 1H, –C(NTMS)*H*), 1.38 (s, 9H, –C(CH_3)$_3$), 0.16 (s, 9H, –Si(CH_3)$_3$).

Thermolysis of (PNP)Ir–N_2 in MTBE. Complex **3** (ca. 10 mg) was dissolved in MTBE (800 μL) and transferred to a resealable NMR tube under a nitrogen atmosphere. The solution was heated at 90 °C for 76 h, and the distribution of products was periodically monitored by ^{31}P NMR (see chart below).[6] After 7 d, the complete disappearance of (PNP)Ir–N_2 and (PNP)Ir=C(H)O^{t}Bu and formation of *trans*-(PNP)Ir(CO)(H)$_2$ were confirmed by ^{1}H and ^{31}P NMR spectroscopy.



Stepwise synthesis of *tert*-butyl *N*-adamantylformimidate. A 30 mL resealable flask was charged with complex **1** (48.6 mg, 0.0687 mmol) and norbornene (31.9 mg, 0.339 mmol) in *tert*-butyl methyl ether (15 mL). AdN_3 (12.2 mg, 0.0688 mmol) was added and the reaction was stirred for 2 h, causing a color change to golden-brown. The solution was irradiated for 30 min, causing a darkening from golden to dark brown, and the reaction allowed to proceed at ambient temperature for 16 h, causing a color change to red-purple. A second equiv of AdN_3 (12.2 mg, 0.0688 mmol) was added and the solution was stirred for 2 h, causing the color to lighten to golden-brown. The sample was subjected to two additional cycles of photolysis and AdN_3 addition, as described above, and volatiles were removed in vacuo, leaving a brownish film. The residues were dissolved in C_6D_6 and the yield of *tert*-butyl *N*-adamantylformimidate (0.256 mmol, 93% based on AdN_3) determined by ^1H NMR spectroscopy via integration relative to an internal standard of hexamethyldisiloxane.

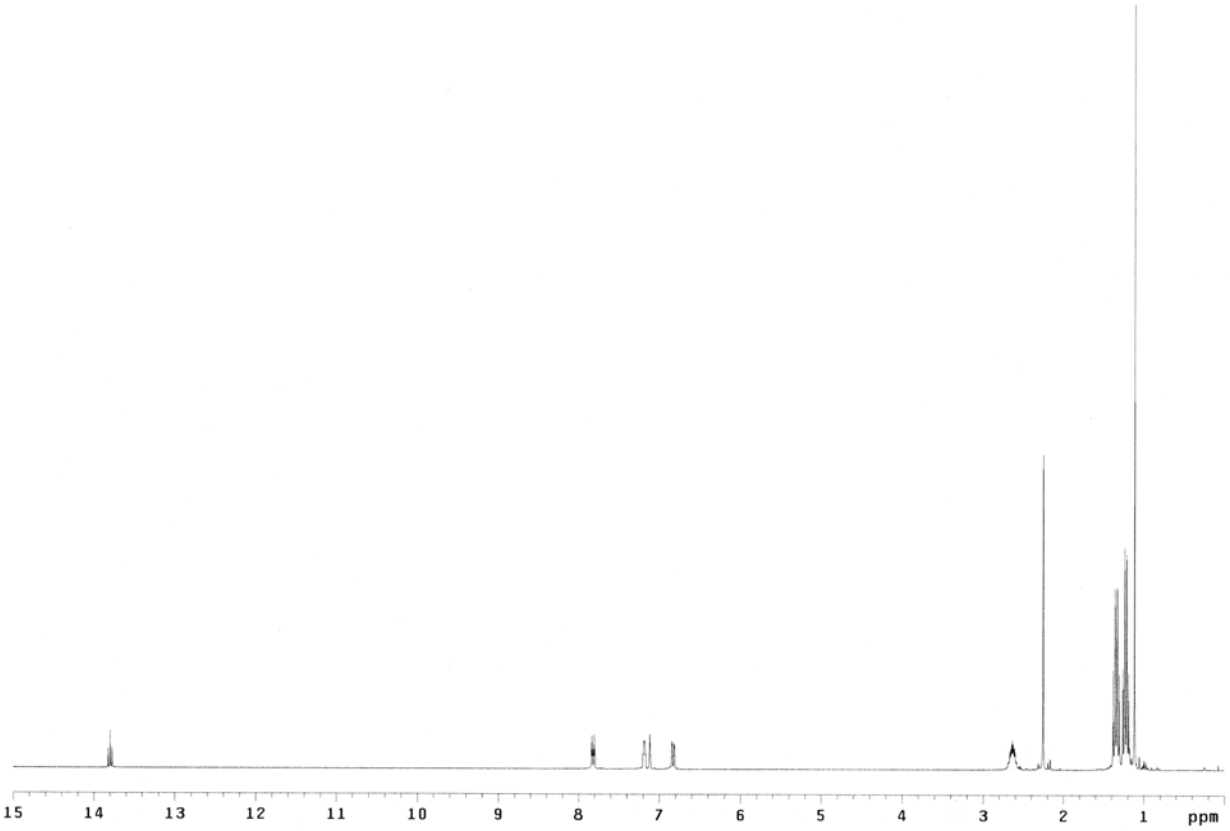


Figure S1. ^{1}H NMR spectrum of (PNP)Ir=C(H)O^{t}Bu (**1**) before reaction with N_2O

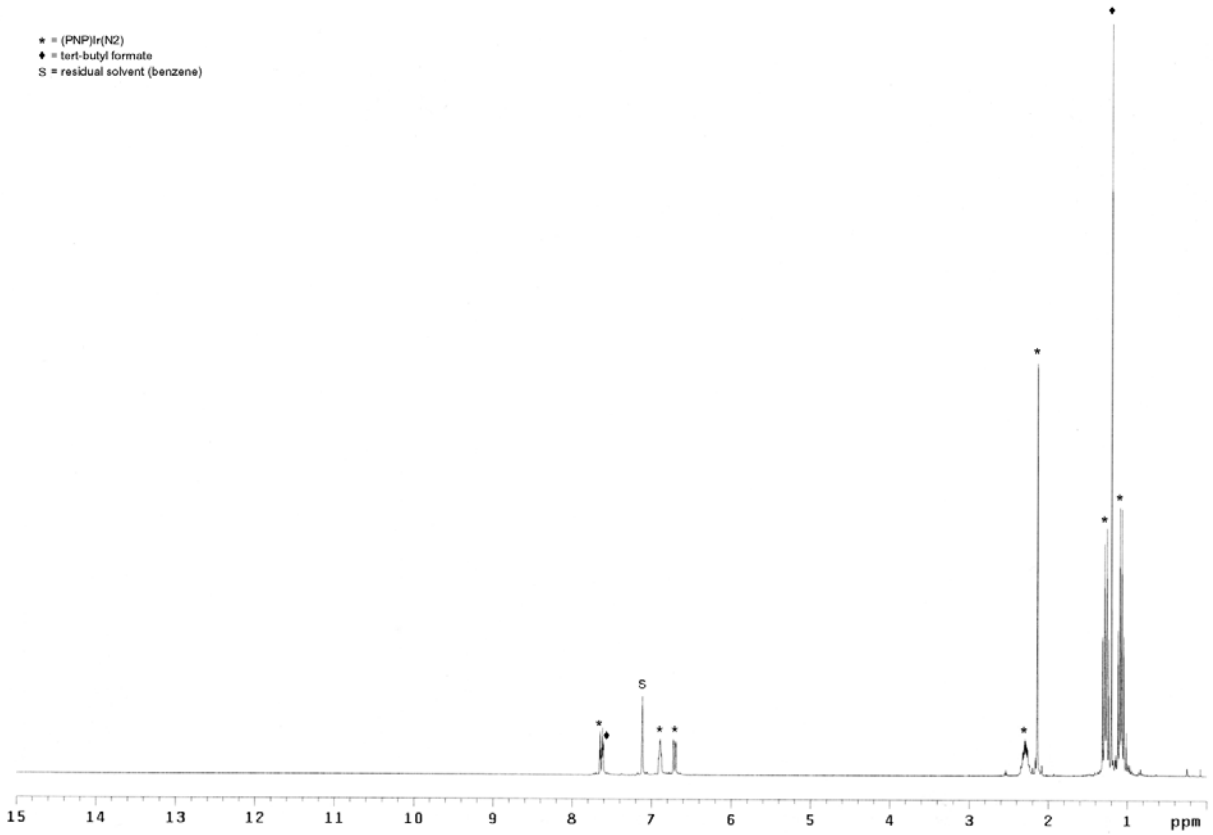


Figure S2. ^{1}H NMR spectrum of crude mixture from reaction of **1** with N_2O (15 min)

References and Notes

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(2) Whited, M. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 5874.
(3) Spencer, L. P.; Altwer, R.; Wei, P.; Gelmini, L.; Gauld, J.; Stephan, D. W. *Organometallics* **2003**, *22*, 3841.
(4) (a) Aue, D. H.; Thomas, D. *J. Org. Chem.* **1974**, *39*, 3855. (b) Aue, D. H.; Thomas, D. *J. Org. Chem.* **1975**, *40*, 2360. (c) Guzmán, A.; Muchowski, J. M.; Naal, N. T. *J. Org. Chem.* **1981**, *46*, 1224.
(5) Romero, P. E.; Whited, M. T.; Grubbs, R. H. *Organometallics* **2008**, *27*, 3422.
(6) For a related study on the thermolysis of (PNP)IrH_2 in MTBE, see reference 5.